Supporting Information

Fused-ring phenazine building blocks for efficient copolymer donors

Wenting Li,‡[a,b] Qishi Liu,‡[b,c] Ke Jin,[b] Ming Cheng,[d] Feng Hao,[e] Wu-Qiang Wu,[f] Shengjian Liu,[g] Zuo Xiao,*[b] Shangfeng Yang,*[c] Shengwei Shi*[a] and Liming Ding*[b]

[a] *School of Materials Science and Engineering, Wuhan Institute of Technology, Wuhan 430205, China. E-mail: shisw@wit.edu.cn*
[b] *Center for Excellence in Nanoscience (CAS), Key Laboratory of Nanosystem and Hierarchical Fabrication (CAS), National Center for Nanoscience and Technology, Beijing 100190, China. E-mail: xiaoz@nanoctr.cn, ding@nanoctr.cn*
[c] *Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, China. E-mail: sfyang@ustc.edu.cn*
[d] *Institute for Energy Research, Jiangsu University, Zhenjiang 212013, China.*
[e] *School of Materials and Energy, University of Electronic Science and Technology of China, Chengdu 611731, China.*
[f] *School of Chemistry, Sun Yat-sen University, Guangzhou 510275, China.*
[g] *School of Chemistry, South China Normal University, Guangzhou 510006, China.*

‡ W. Li and Q. Liu contributed equally to this work.

1. General characterization

^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance-400 spectrometer. Absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Cyclic voltammetry was done by using a Shanghai Chenhua CHI620D voltammetric analyzer under argon in an anhydrous acetonitrile solution of tetra-n-butylammonium hexafluorophosphate (0.1 M). A glassy-carbon electrode was used as the working electrode, a platinum-wire was used as the counter electrode, and a Ag/Ag$^+$ electrode was used as the reference electrode. P1 (or P2) was coated onto glassy-carbon electrode and all potentials were corrected against Fc/Fc$^+$. AFM was performed on a Multimode microscope (Veeco) using tapping mode.

2. Synthesis

All reagents were purchased from J&K Co., Aladdin Co., Innochem Co., Derthon Co., SunaTech Co. and other commercial suppliers. Y6 was purchased from eFlexPV Co. Benzo[2,1-b:3,4-b']dithiophene-4,5-dione was purchased from Henan Psai Co. All reactions dealing with air- or moisture-sensitive compounds were carried out by using standard Schlenk techniques.

Compound 1. To a solution of benzo[2,1-b:3,4-b']dithiophene-4,5-dione (220 mg, 1 mmol) in a mixed solvent of $CHCl_3$ (8 mL) and AcOH (4 mL) was added NBS (356 mg, 2 mmol). The mixture was stirred at room temperature for 24 h and then poured into water followed by extraction with CH_2Cl_2 three times. The combined organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using CH_2Cl_2:petroleum ether (1:1) as eluent to give **compound 1** as a black solid (250 mg, 66%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.46 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 172.54, 143.58, 135.37, 130.01, 114.60. MALDI-TOF MS (m/z): 378.8 (M + H$^+$).

DTPz-Br. To a solution of compound 1 (189 mg, 0.5 mmol) and benzene-1,2-diamine (65 mg, 0.6 mmol) in $CHCl_3$ (8 mL) was added AcOH (1 mL). The mixture was stirred at 65 °C for 2 h and then poured into MeOH. The precipitate was collected and dried under vacuum to give **DTPz-Br** as a yellow solid (218 mg, 97%). NMR data were not acquired due to the extremely low solubility of DTPz-Br. MALDI-TOF MS (m/z): 451.7 (M + H$^+$).

FDTPz-Br. To a solution of compound 1 (189 mg, 0.5 mmol) and 4,5-difluorobenzene-1,2-diamine (86 mg, 0.6 mmol) in $CHCl_3$ (8 mL) was added AcOH (1 mL). The mixture was stirred at 65 °C for 2h and then poured into MeOH. The precipitate was collected and dried under vacuum to give **FDTPz-Br** as a yellow solid (236 mg, 97%). NMR data were not acquired due to the extremely low solubility of FDTPz-Br. MALDI-TOF MS (m/z): 487.7 ($M + H^+$).

Compound 2a. To a solution of DTPz-Br (90 mg, 0.2 mmol) and (4-(2-hexyldecyl)thiophen-2-yl)trimethylstannane (226 mg, 0.48 mmol) in toluene (5 mL) and DMF (1 mL) was added $Pd(PPh_3)_4$ (23 mg, 0.02 mmol) under N_2. The mixture was heated to reflux and stirred overnight. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using CH_2Cl_2:petroleum ether (1:2) as eluent to give **compound 2a** as a red oil (157 mg, 87%). ^1H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.39 (s, 2H), 8.29-8.31(m, 2H), 7.85-7.86 (m, 2H), 7.19 (s, 2H), 6.90 (s, 2H), 2.58 (d, J = 6.6 Hz, 4H), 1.67 (s, 2H), 1.29 (br, 48H), 0.86-0.92 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 142.95, 141.49, 139.15, 136.67, 136.33, 135.21, 133.55, 129.37, 129.26, 126.53, 121.06, 119.87, 38.88, 35.00, 33.36, 33.34, 31.95, 30.08, 29.75, 29.70, 29.40, 26.66, 26.64, 22.73, 22.72, 14.16, 14.14. MALDI-TOF MS (m/z): 906.7 ($M + H^+$).

Compound 2b. To a solution of FDTPz-Br (97 mg, 0.2 mmol) and (4-(2-hexyldecyl)thiophen-2-yl)trimethylstannane (226 mg, 0.48 mmol) in toluene (5 mL) and DMF (1 mL) was added $Pd(PPh_3)_4$ (23 mg, 0.02 mmol) under N_2. The mixture was heated to reflux and stirred overnight. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using CH_2Cl_2:petroleum ether (1:2) as eluent to give **compound 2b** as a red oil (135 mg, 72%). ^1H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.22 (s, 2H), 7.95 (t, J = 9.3 Hz, 2H), 7.14 (s, 2H), 6.90 (s, 2H), 2.57 (d, J = 6.6 Hz, 4H), 1.67 (s, 2H), 1.30 (br, 48H), 0.86-0.92 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 153.77, 153.58, 151.19, 151.00, 142.92, 138.55, 138.50, 138.39, 136.78, 136.00, 134.34, 133.23, 126.46, 121.09, 119.10, 113.97, 113.85, 113.79, 38.86, 34.94, 33.34, 31.99, 31.97, 30.11, 29.78, 29.73, 29.42, 26.66, 26.64, 22.76, 22.73, 14.18, 14.15. MALDI-TOF MS (m/z): 941.7 ($M + H^+$).

Compound 3a. To a solution of compound 2a (91 mg, 0.1 mmol) in $CHCl_3$ (10 mL) was added NBS (36 mg, 0.2 mmol) at room temperature. The mixture was stirred for 2 h. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using CH_2Cl_2:petroleum ether (1:2) as eluent to give

compound 3a as a red solid (98 mg, 92%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.28 (br, 4H), 7.84 (d, *J* = 7.6 Hz, 2H), 6.99 (s, 2H), 2.52 (d, *J* = 6.9 Hz, 4H), 1.72 (s, 2H), 1.30 (br, 48H), 0.86-0.91 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 142.24, 141.35, 138.67, 136.01, 135.54, 135.10, 133.02, 129.34, 129.17, 125.66, 119.76, 109.68, 38.55, 34.22, 33.37, 33.35, 31.96, 30.10, 29.77, 29.71, 29.42, 26.55, 22.75, 22.73, 14.19, 14.16. MALDI-TOF MS (m/z): 1064.5 ($M + H^+$).

Compound 3b. To a solution of compound 2b (94 mg, 0.1 mmol) in $CHCl_3$ (10 mL) was added NBS (36 mg, 0.2 mmol) at room temperature. The mixture was stirred for 2 h. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using CH_2Cl_2:petroleum ether (1:2) as eluent to give **compound 3b** as a red solid (103 mg, 94%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.19 (s, 2H), 7.96 (t, *J* = 9.3 Hz, 2H), 6.98 (s, 2H), 2.53 (d, *J* = 7.1 Hz, 4H), 1.72 (s, 2H), 1.29 (br, 48H), 0.86-0.92 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 153.87, 153.69, 151.28, 151.10, 142.36, 138.49, 138.14, 135.80, 135.61, 134.39, 132.97, 125.71, 119.16, 113.80, 110.01, 38.54, 34.18, 33.34, 31.97, 30.11, 29.78, 29.72, 29.43, 26.54, 26.52, 22.76, 22.74, 14.20, 14.16. MALDI-TOF MS (m/z): 1100.5 ($M + H^+$).

P1. To a mixture of compound 3a (53.2 mg, 0.050 mmol), ClBDT-Sn (48.6 mg, 0.050 mmol), $Pd_2(dba)_3$ (1.8 mg, 0.0020 mmol) and $P(o\text{-}Tol)_3$ (4.9 mg, 0.016 mmol) in a Schlenk flask was added toluene (1.2 mL) under argon. The mixture was heated to reflux for 20 h. Then the solution was cooled to room temperature and added into 100 mL methanol dropwise. The precipitate was collected and further purified via Soxhlet extraction by using methanol, hexane and chloroform in sequence. The chloroform fraction was concentrated and added into methanol dropwise. The precipitate was collected and dried under vacuum overnight to give **P1** as a black solid (63 mg, 81%). The M_n for P1 is 53.5 kDa, with a PDI of 2.35. ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 6.75-8.33 (br, aromatic protons), 2.86-3.07 (br, aliphatic protons), 0.78-1.68 (br, aliphatic protons).

P2. To a mixture of compound 3b (55.0 mg, 0.050 mmol), Cl-BDT-Sn (48.6 mg, 0.050 mmol), $Pd_2(dba)_3$ (1.8 mg, 0.0020 mmol) and $P(o\text{-}Tol)_3$ (4.9 mg, 0.016 mmol) in a Schlenk flask was added toluene (1 mL) under argon. The mixture was heated to reflux for 24 h. Then the solution was cooled to room temperature and added into 100 mL methanol dropwise. The precipitate was collected and further purified via Soxhlet extraction by using methanol, hexane and chloroform in sequence. The chloroform fraction was concentrated and added into methanol dropwise. The precipitate was collected and dried under vacuum overnight to give **P2** as a black solid (58 mg, 73%).

The M_n for P2 is 55.2 kDa, with a PDI of 1.82. ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 6.78-8.38 (br, aromatic protons), 2.86-3.06 (br, aliphatic protons), 0.78-1.66 (br, aliphatic protons).

3. NMR

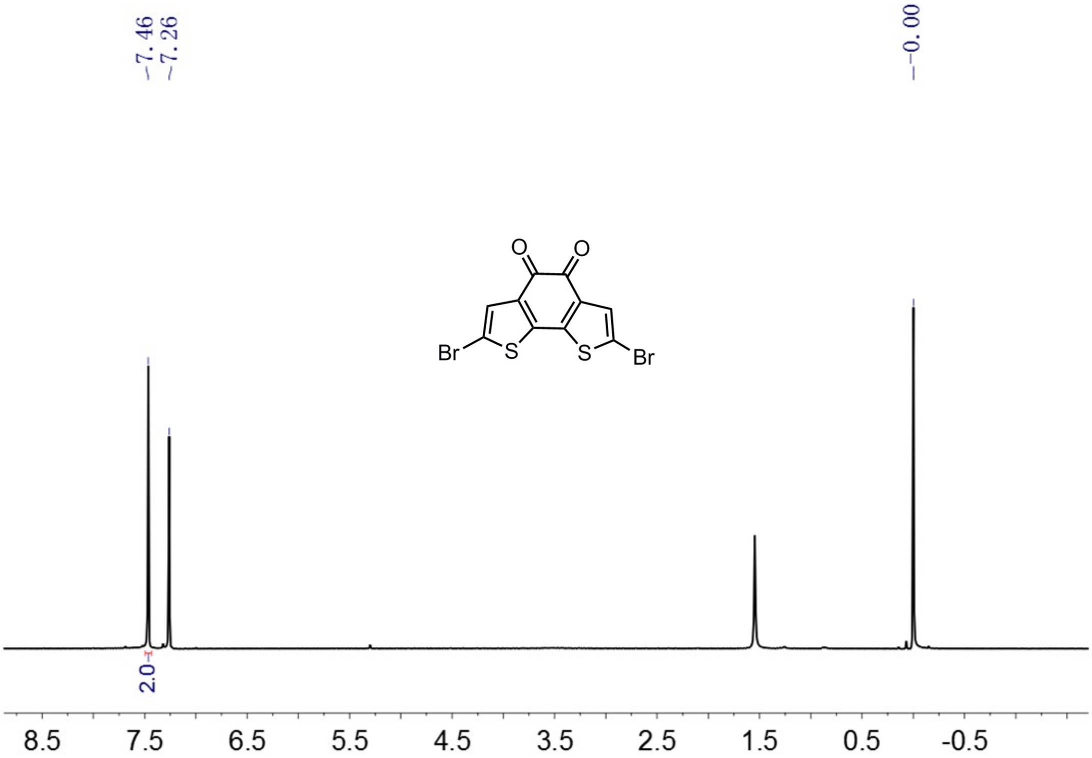

Fig. S1 ^{1}H NMR spectrum of **compound 1**.

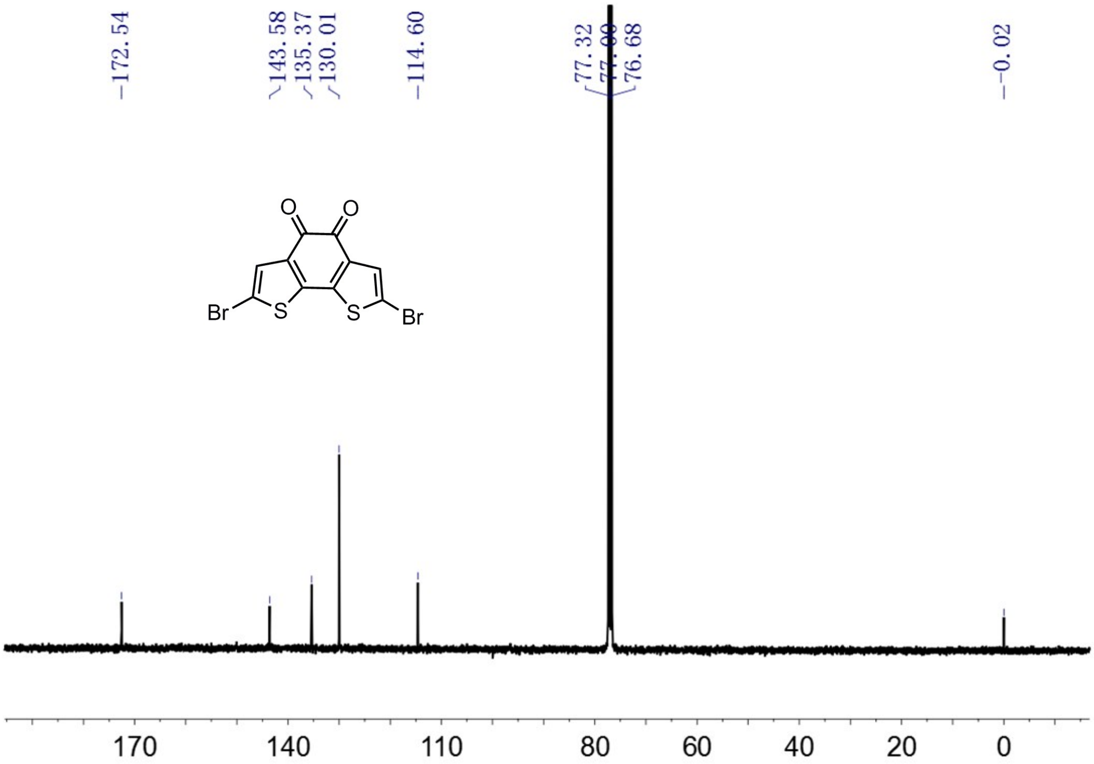

Fig. S2 ^{13}C NMR spectrum of **compound 1**.

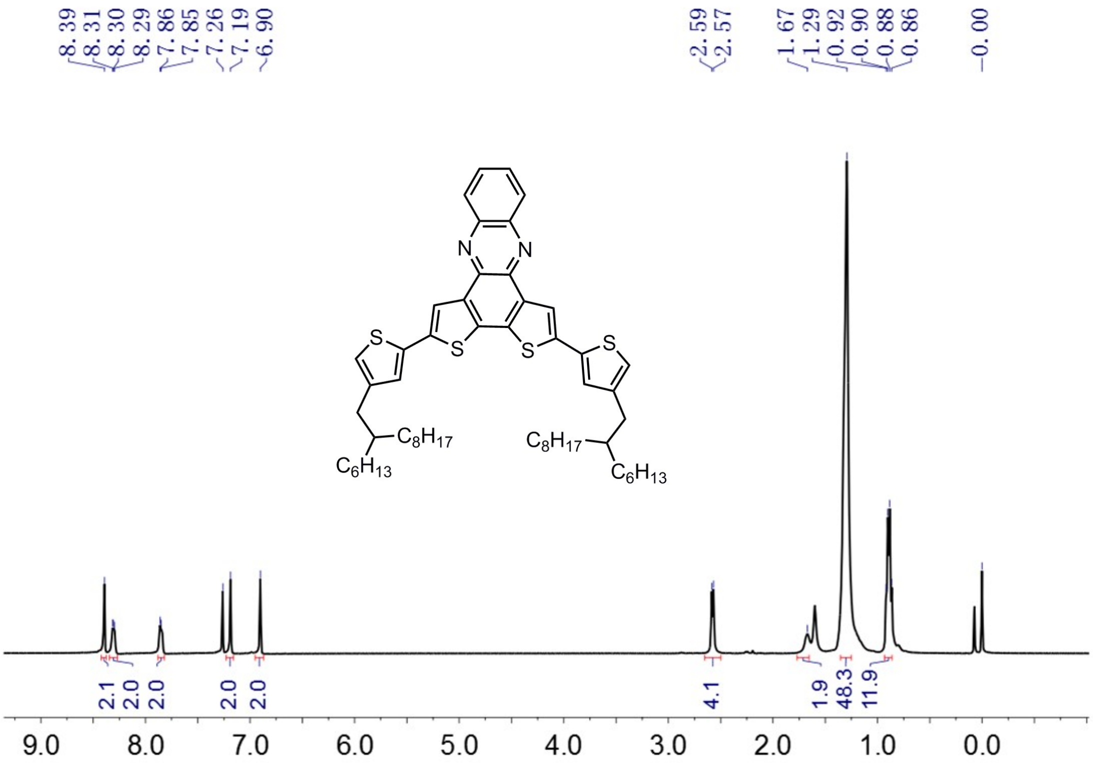

Fig. S3 ^{1}H NMR spectrum of **compound 2a**.

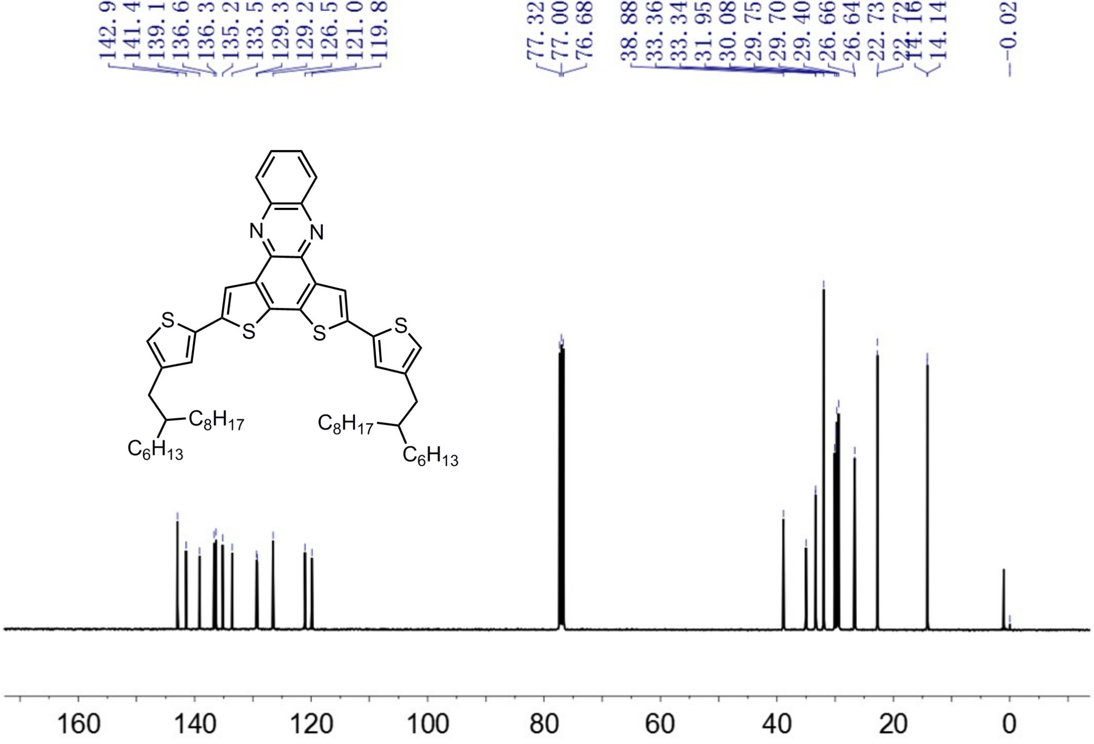

Fig. S4 ^{13}C NMR spectrum of **compound 2a**.

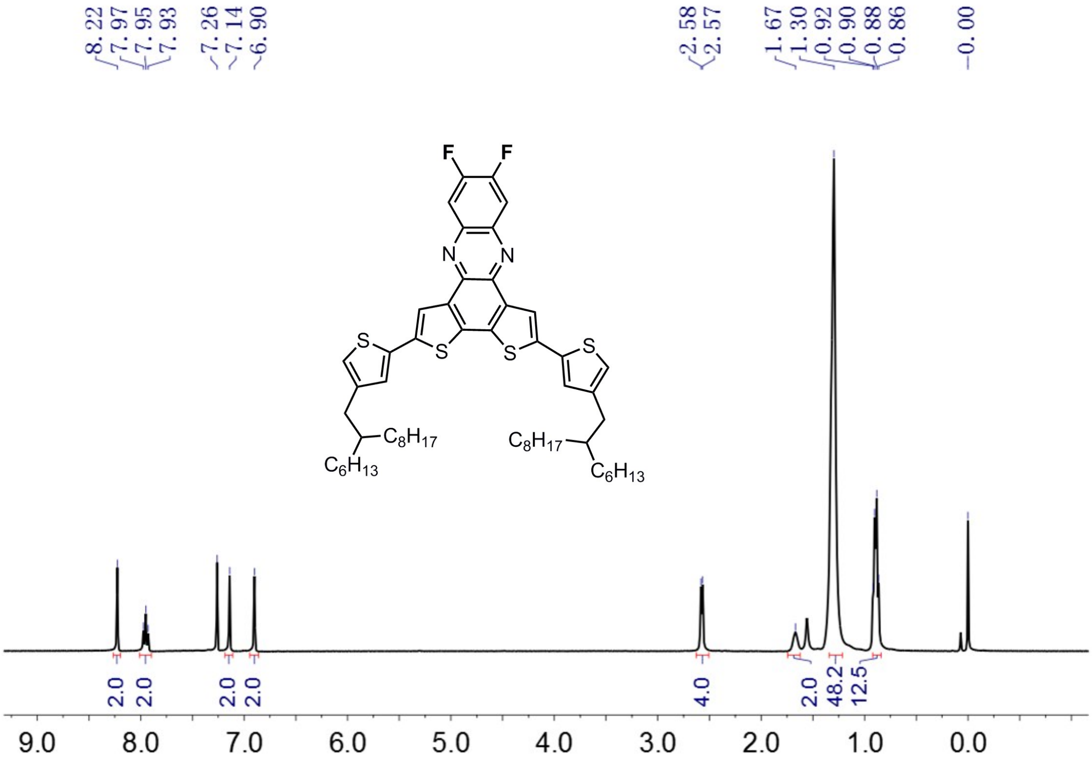

Fig. S5 ^{1}H NMR spectrum of **compound 2b**.

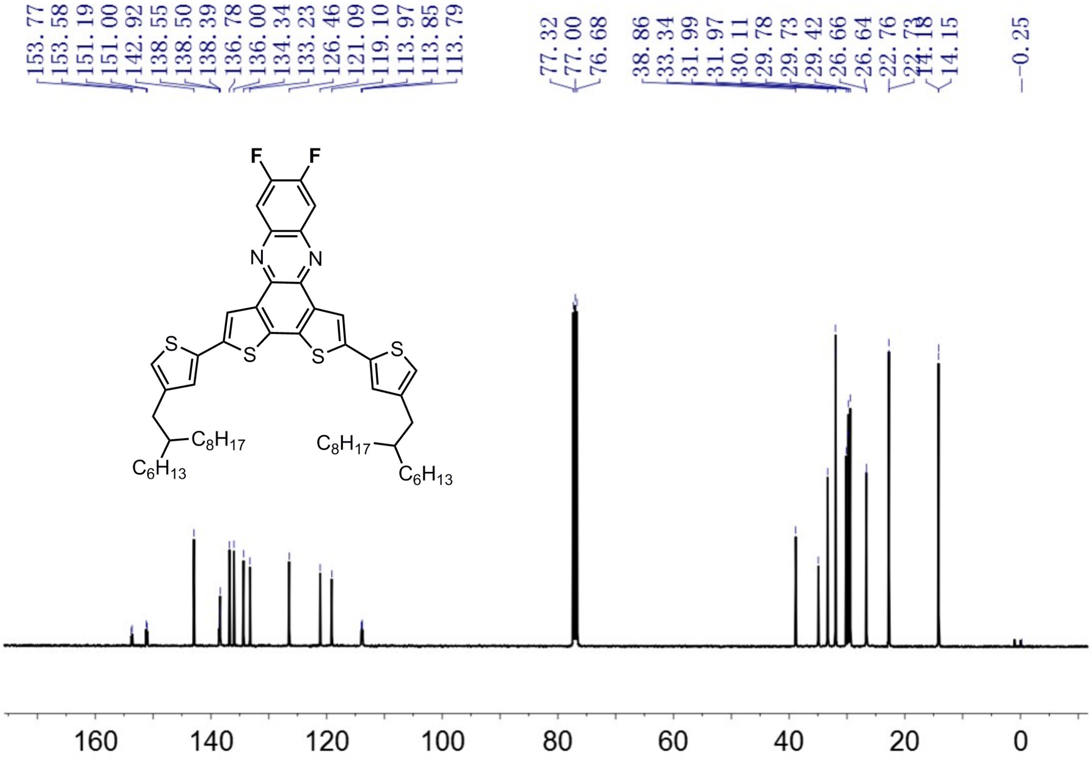

Fig. S6 ^{13}C NMR spectrum of **compound 2b**.

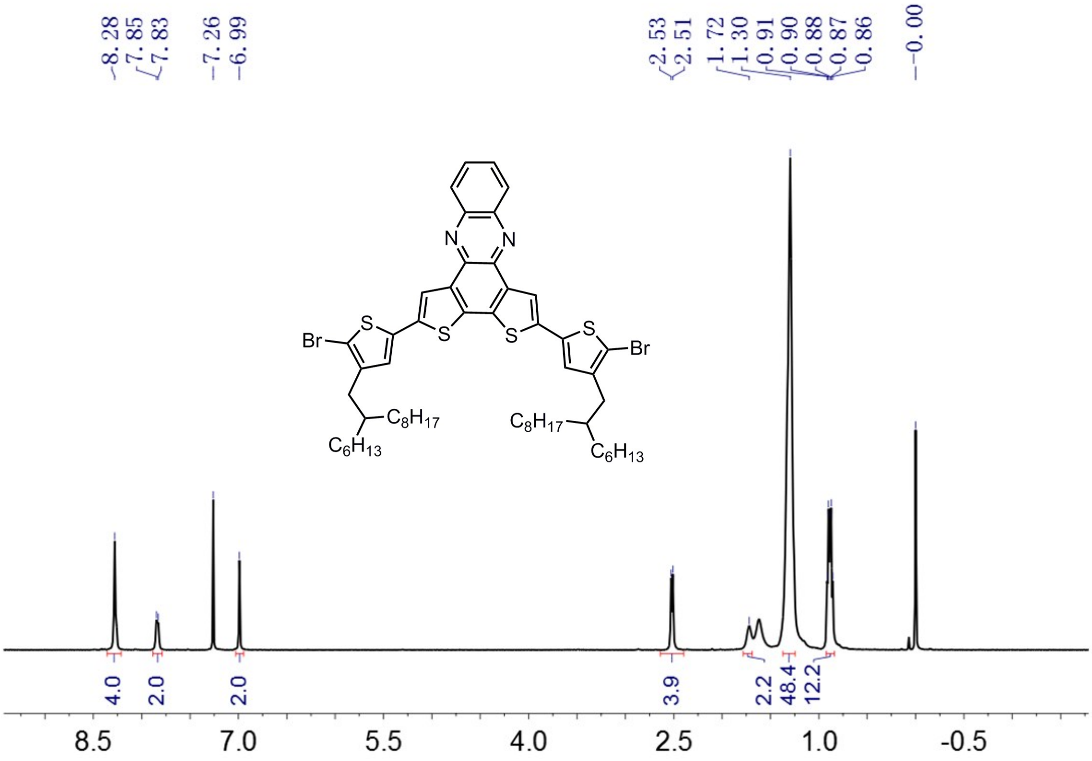

Fig. S7 ^{1}H NMR spectrum of **compound 3a**.

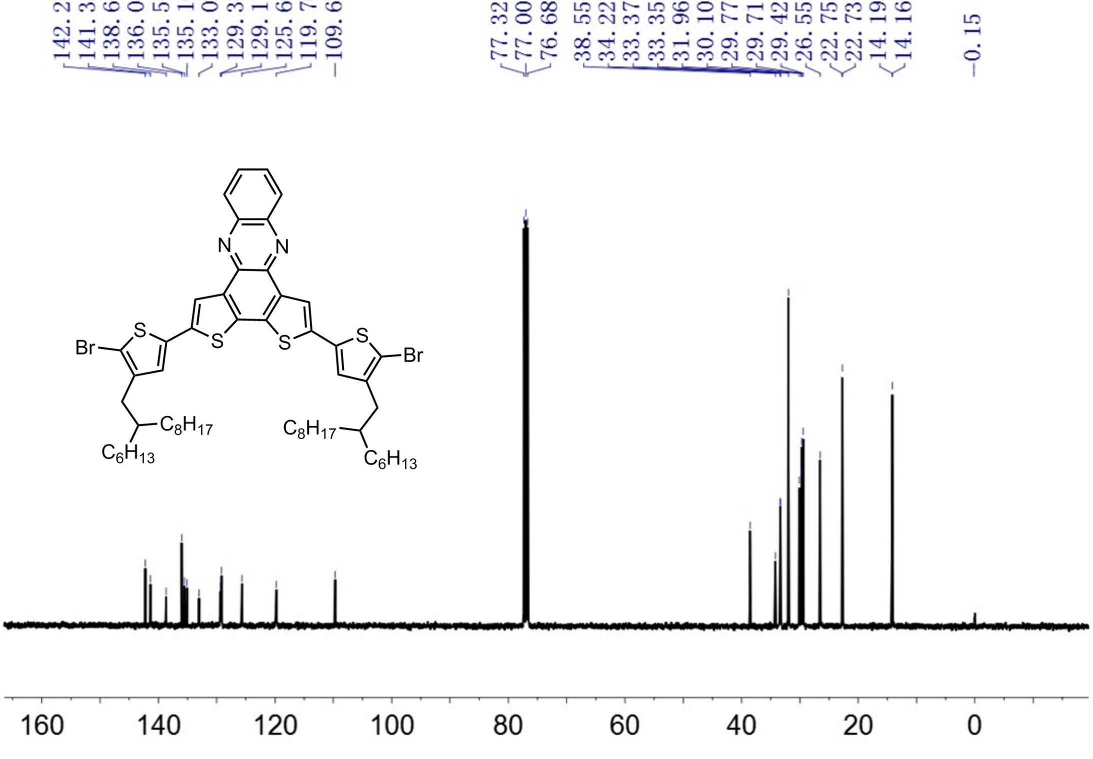

Fig. S8 ^{13}C NMR spectrum of **compound 3a**.

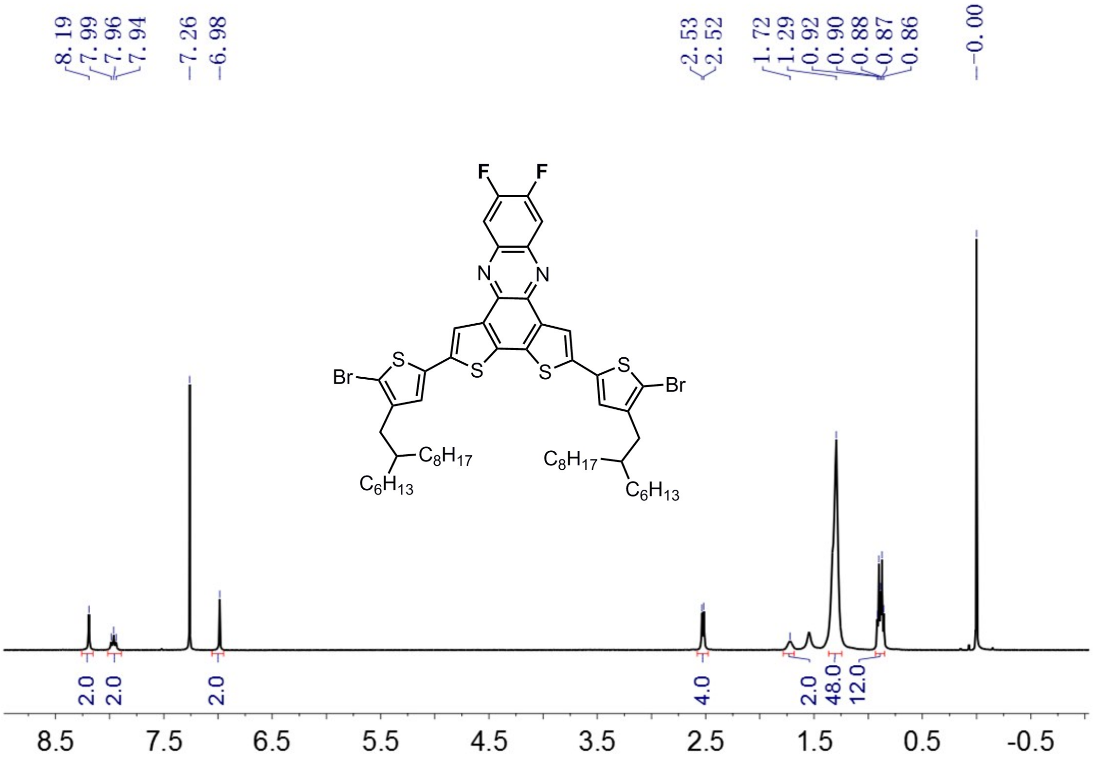

Fig. S9 ^{1}H NMR spectrum of **compound 3b**.

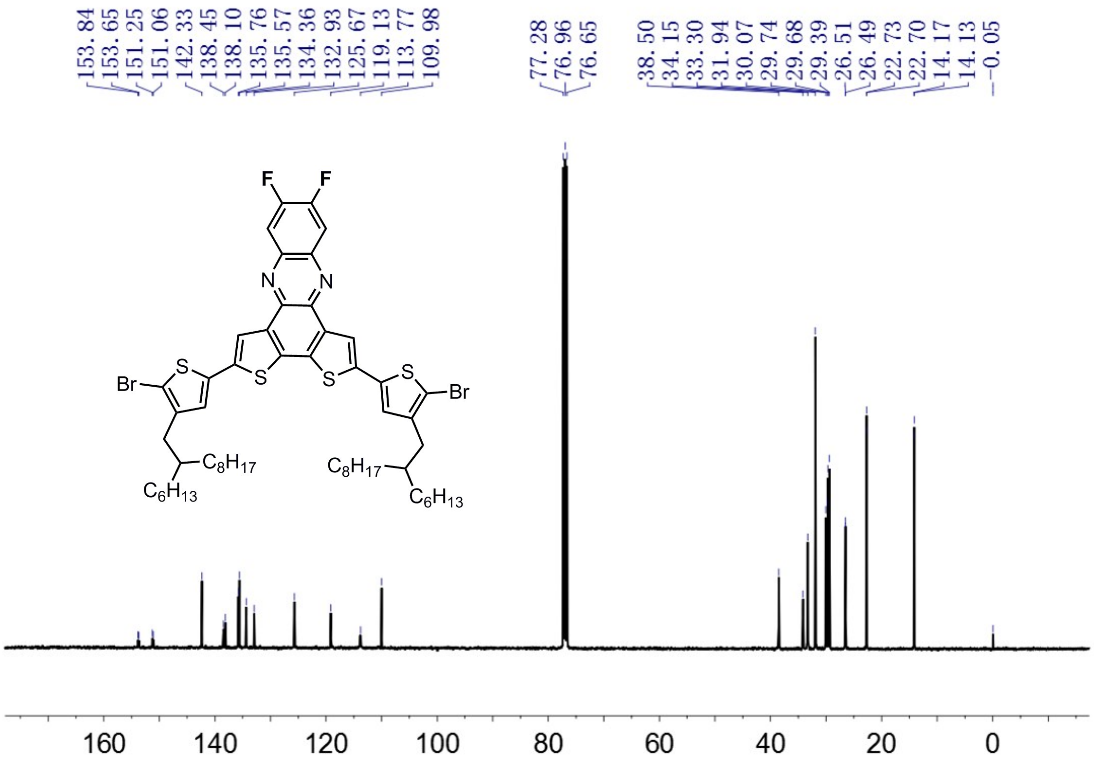

Fig. S10 ^{13}C NMR spectrum of **compound 3b**.

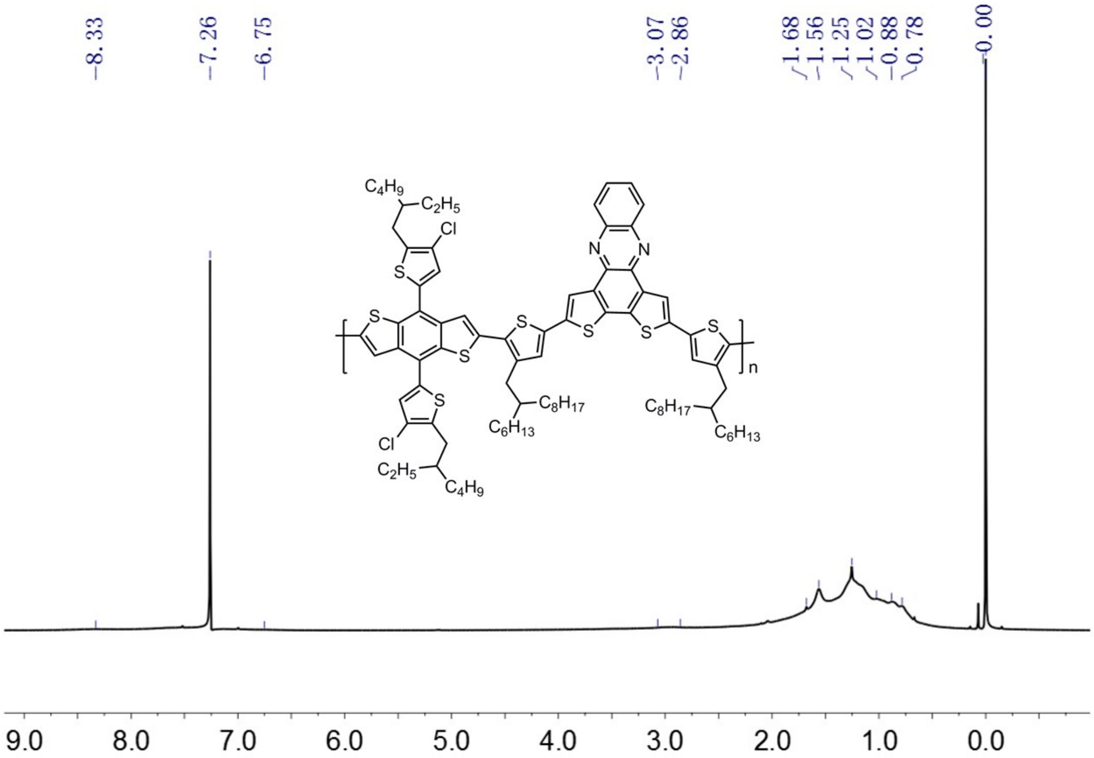

Fig. S11 ^{1}H NMR spectrum of **P1**.

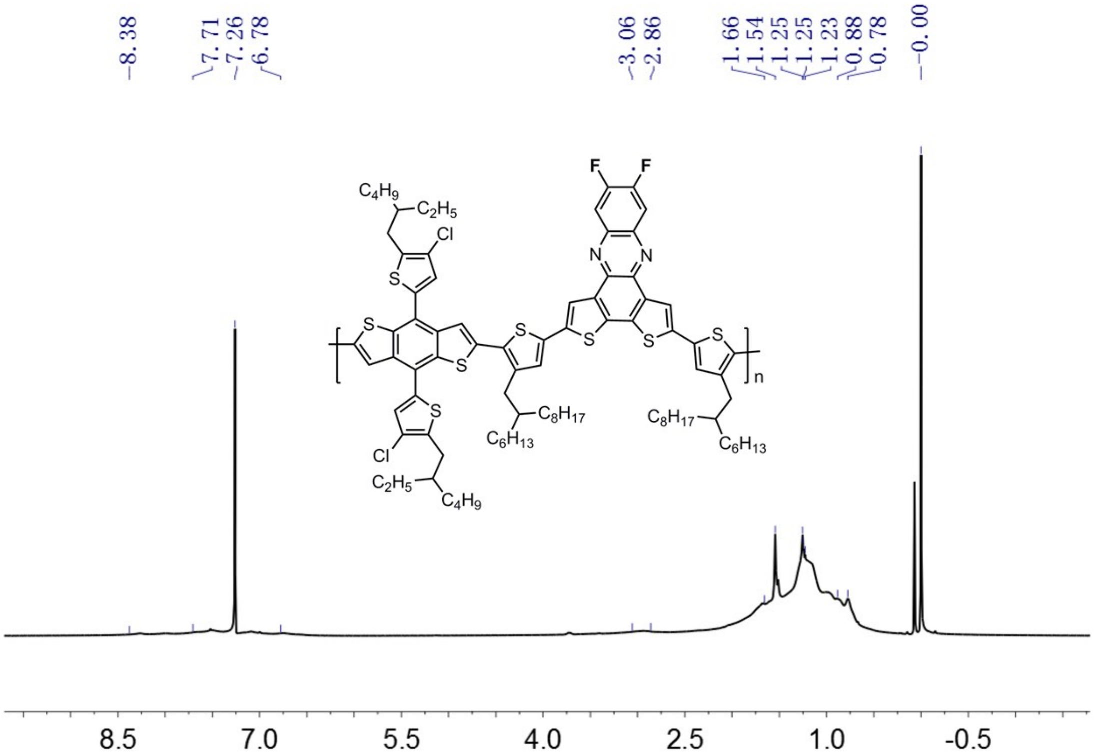

Fig. S12 ^{1}H NMR spectrum of **P2**.

4. Absorption spectra

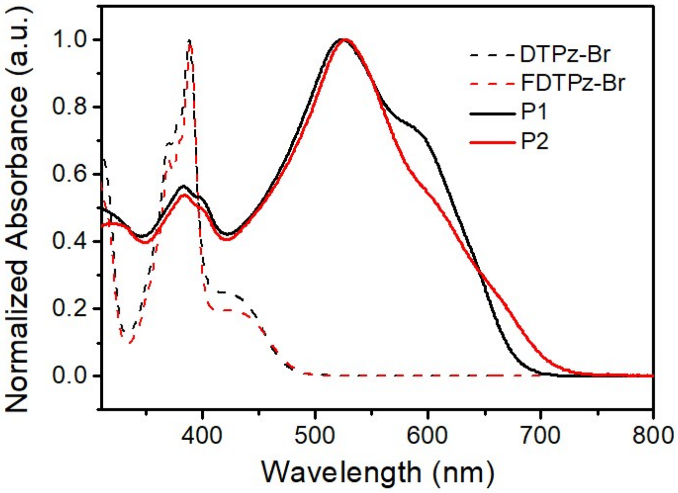

Fig. S13 Absorption spectra for DTPz-Br, FDTPz-Br, P1 and P2 in $CHCl_3$.

5. CV

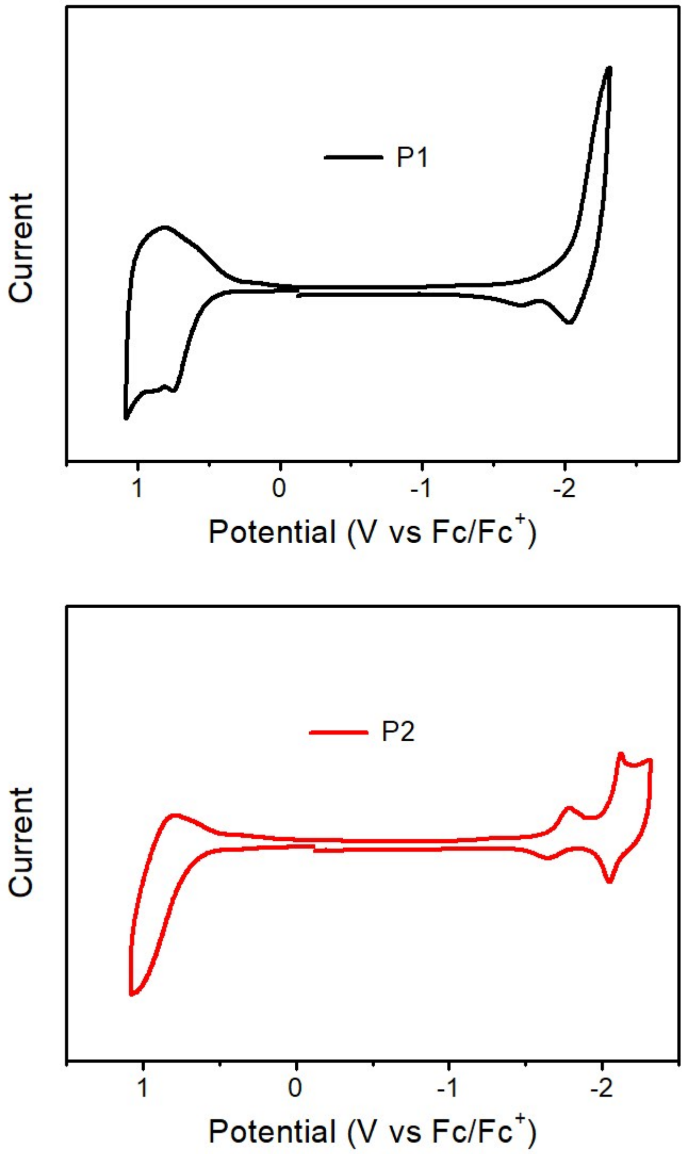

Fig. S14 Cyclic voltammograms for P1 and P2.

6. Device fabrication and measurements

Conventional solar cells

A 30 nm thick PEDOT:PSS layer was made by spin-coating an aqueous dispersion onto ITO glass (4000 rpm for 30 s). PEDOT:PSS substrates were dried at 150 °C for 10 min. A P1:Y6 (or P2:Y6) blend in chloroform (CF) with diphenyl ether (DPE) was spin-coated onto PEDOT:PSS. PDINO (1 mg/mL) in MeOH was spin-coated onto active layer (3000 rpm for 40 s). Al (~100 nm) was evaporated onto PDINO through a shadow mask (pressure ca. 10^{-4} Pa). The effective area for the devices is 4 mm^2. The thicknesses of the active layers were measured by using a KLA Tencor D-120 profilometer. J-V curves were measured by using a computerized Keithley 2400 SourceMeter and a Xenon-lamp-based solar simulator (Enli Tech, AM 1.5G, 100 mW/cm^2). The illumination intensity of solar simulator was determined by using a monocrystalline silicon solar cell (Enli SRC2020, 2 cm×2 cm) calibrated by NIM. The external quantum efficiency (EQE) spectra were measured by using a QE-R3011 measurement system (Enli Tech).

Hole-only devices

The structure for hole-only devices is ITO/PEDOT:PSS/active layer/MoO_3/Al. A 30 nm thick PEDOT:PSS layer was made by spin-coating an aqueous dispersion onto ITO glass (4000 rpm for 30 s). PEDOT:PSS substrates were dried at 150 °C for 10 min. A pure P1 (or P2) in CF or a P1:Y6 (or P2:Y6) blend in CF with DPE was spin-coated onto PEDOT:PSS. Finally, MoO_3 (~6 nm) and Al (~100 nm) was successively evaporated onto the active layer through a shadow mask (pressure ca. 10^{-4} Pa). J-V curves were measured by using a computerized Keithley 2400 SourceMeter in the dark.

Electron-only devices

The structure for electron-only devices is Al/active layer/Ca/Al. Al (~80 nm) was evaporated onto a glass substrate. A P1:Y6 (or P2:Y6) blend in CF with DPE was spin-coated onto Al. Ca (~5 nm) and Al (~100 nm) were successively evaporated onto the active layer through a shadow mask (pressure ca. 10^{-4} Pa). J-V curves were measured by using a computerized Keithley 2400 SourceMeter in the dark.

7. Optimization of device performance

Table S1 Optimization of D/A ratio for P1:Y6 conventional solar cells.[a]

D/A [w/w]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
1:1	0.784	24.74	52.4	10.16 (9.96)[b]
1:1.2	0.782	25.97	58.4	11.85 (11.52)
1:1.4	0.780	25.35	60.4	11.94 (11.49)
1:1.6	0.777	25.70	61.6	12.30 (11.85)
1:1.8	0.782	24.27	61.0	11.59 (11.07)

[a] Blend solution: 20 mg/mL in CF with 1 vol% DPE; spin-coating: 5000 rpm for 30 s.
[b] Data in parentheses are averages for 8 cells.

Table S2 Optimization of active layer thickness for P1:Y6 conventional solar cells.[a]

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
121	0.774	26.20	58.3	11.81 (11.46)[b]
99	0.777	25.70	61.6	12.30 (11.85)
82	0.772	24.25	64.8	12.12 (11.67)
69	0.773	21.23	66.5	10.91 (10.85)

[a] D/A ratio: 1:1.6 (w/w); blend solution: 20 mg/mL in CF with 1 vol% DPE.
[b] Data in parentheses are averages for 8 cells.

Table S3 Optimization of DPE content for P1:Y6 conventional solar cells.[a]

DPE [vol%]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
0	0.798	24.79	59.2	11.71 (11.49)[b]
0.5	0.780	25.64	60.3	12.08 (11.64)
1	0.777	25.70	61.6	12.30 (11.85)
1.5	0.760	26.15	59.0	11.73 (11.53)

[a] D/A ratio: 1:1.6 (w/w); blend solution: 20 mg/mL in CF; spin-coating: 5000 rpm for 30 s.

[b] Data in parentheses are averages for 8 cells.

Table S4 Optimization of D/A ratio for P2:Y6 conventional solar cells.[a]

D/A [w/w]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
1:1	0.878	26.12	63.5	14.56 (14.02)[b]
1:1.2	0.879	25.84	64.9	14.74 (14.27)
1:1.4	0.867	26.53	65.8	15.14 (14.99)
1:1.6	0.867	25.72	65.8	14.66 (14.20)
1:1.8	0.863	25.75	60.9	13.53 (13.18)

[a] Blend solution: 20 mg/mL in CF with 1 vol% DPE; spin-coating: 5000 rpm for 30 s.

[b] Data in parentheses are averages for 8 cells.

Table S5 Optimization of active layer thickness for P2:Y6 conventional solar cells.[a]

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
118	0.864	26.12	64.3	14.51 (14.35)[b]
101	0.867	26.53	65.8	15.14 (14.99)
85	0.870	25.07	66.9	14.59 (14.58)
74	0.871	24.52	67.9	14.51 (14.46)

[a] D/A ratio: 1:1.4 (w/w); blend solution: 20 mg/mL in CF with 1 vol% DPE.

[b] Data in parentheses are averages for 8 cells.

Table S6 Optimization of DPE content for P2:Y6 conventional solar cells.[a]

DPE [vol%]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
0	0.888	23.67	64.8	13.63 (13.33)[b]
0.5	0.876	24.45	66.2	14.18 (13.94)
1	0.867	26.53	65.8	15.14 (14.99)
1.5	0.863	25.09	66.8	14.46 (13.95)

[a] D/A ratio: 1:1.4 (w/w); blend solution: 20 mg/mL in CF; spin-coating: 5000 rpm for 30 s.

[b] Data in parentheses are averages for 8 cells.

8. Exciton dissociation probabilities

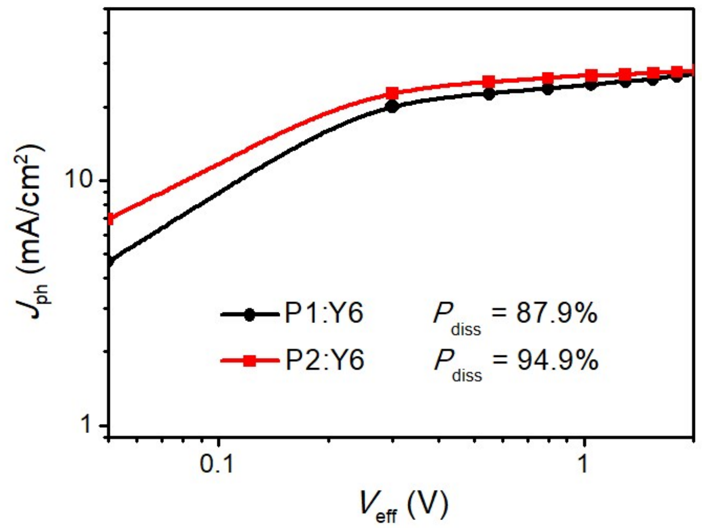

Fig. S15 J_{ph}-V_{eff} plots.

9. Bimolecular recombination

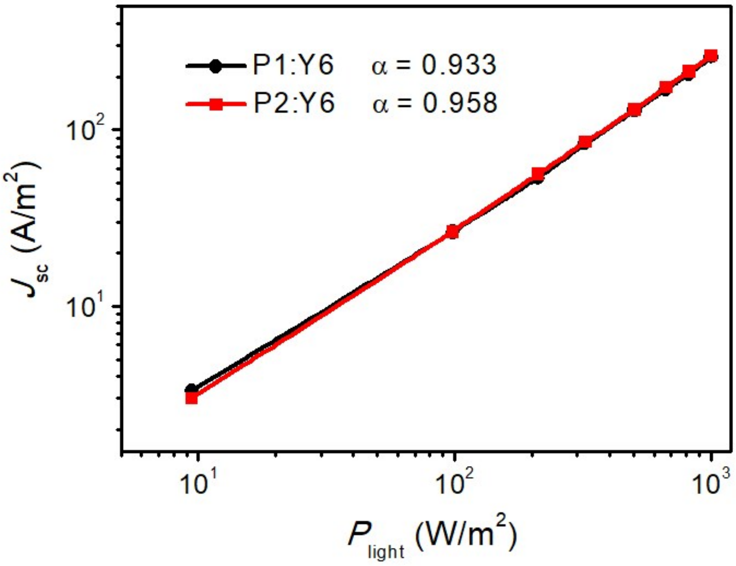

Fig. S16 J_{sc}-P_{light} plots.

10. SCLC

Charge carrier mobility was measured by SCLC method. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by:

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{V^2}{d^3}$$

where J is the current density, μ is the zero-field mobility of holes (μ_{h}) or electrons (μ_{e}), ε_0 is the permittivity of the vacuum, ε_{r} is the relative permittivity of the material, d is the thickness of the blend film, and V is the effective voltage ($V = V_{\mathrm{appl}} - V_{\mathrm{bi}}$, where V_{appl} is the applied voltage, and V_{bi} is the built-in potential determined by electrode work function difference). Here, $V_{\mathrm{bi}} = 0.1$ V for hole-only devices, $V_{\mathrm{bi}} = 0$ V for electron-only devices.[1] The mobility was calculated from the slope of $J^{1/2}$-V plots.

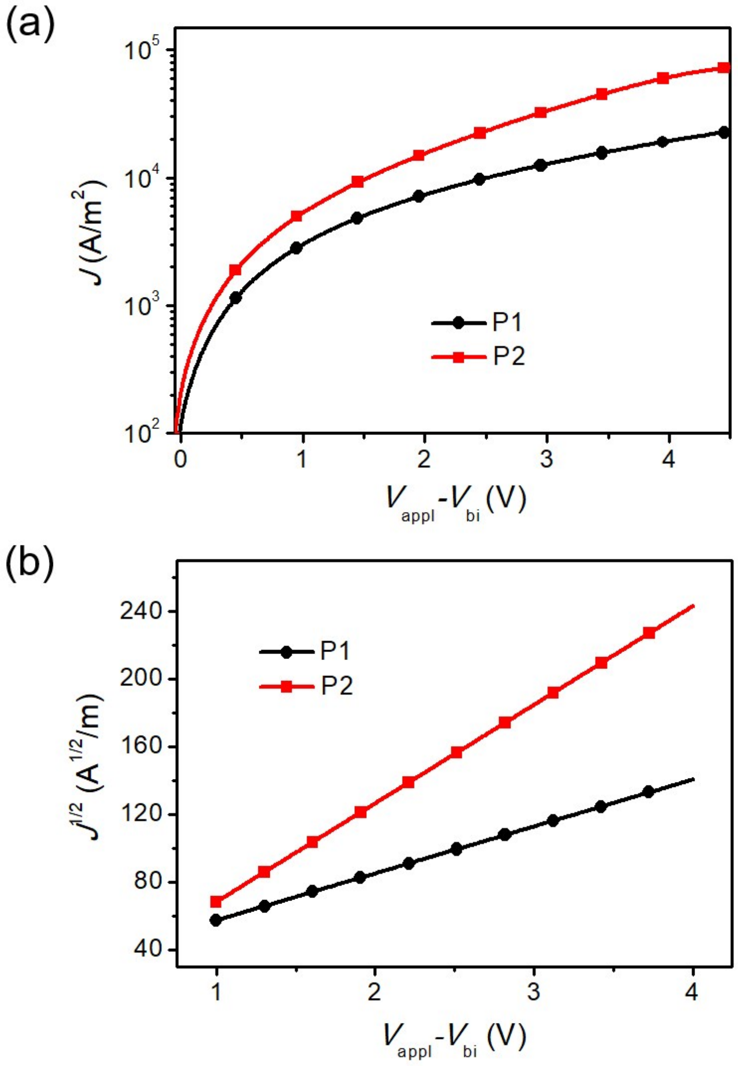

Fig. S17 J-V curves (a) and corresponding $J^{1/2}$-V plots (b) for the hole-only devices (in dark). The thicknesses for P1 and P2 pure films are 92 nm and 88 nm, respectively.

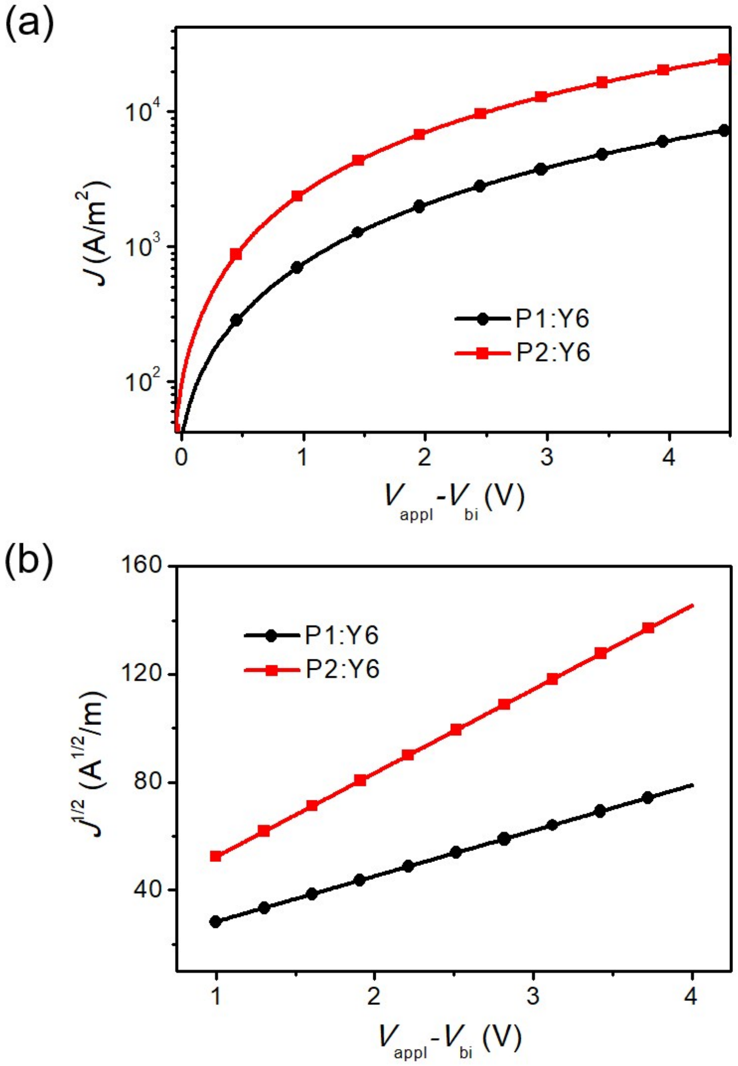

Fig. S18 *J*-*V* curves (a) and corresponding $J^{1/2}$-V plots (b) for the hole-only devices (in dark). The thicknesses for P1:Y6 (1:1.6) film (1 vol% DPE) and P2:Y6 (1:1.4) film (1 vol% DPE) are 112 nm and 102 nm, respectively.

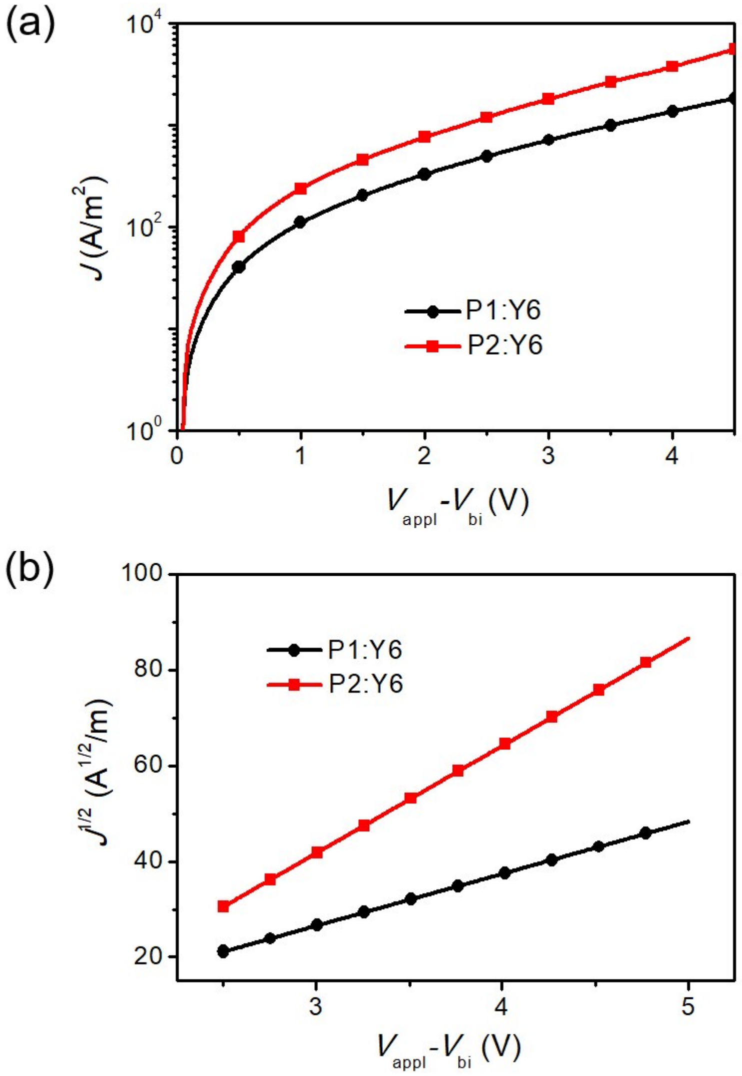

Fig. S19 J-V curves (a) and corresponding $J^{1/2}$-V plots (b) for the electron-only devices (in dark). The thicknesses for P1:Y6 (1:1.6) film (1 vol% DPE) and P2:Y6 (1:1.4) film (1 vol% DPE) are 120 nm and 113 nm, respectively.

Table S7 Hole and electron mobilities.

Films	μ_h [cm^2/Vs]	μ_e [cm^2/Vs]	μ_h/μ_e
P1	2.00×10^{-4}	-	-
P2	7.74×10^{-4}	-	-
P1:Y6 (1:1.6)	1.33×10^{-4}	6.81×10^{-5}	1.95
P2:Y6 (1:1.4)	3.42×10^{-4}	2.42×10^{-4}	1.41

11. AFM

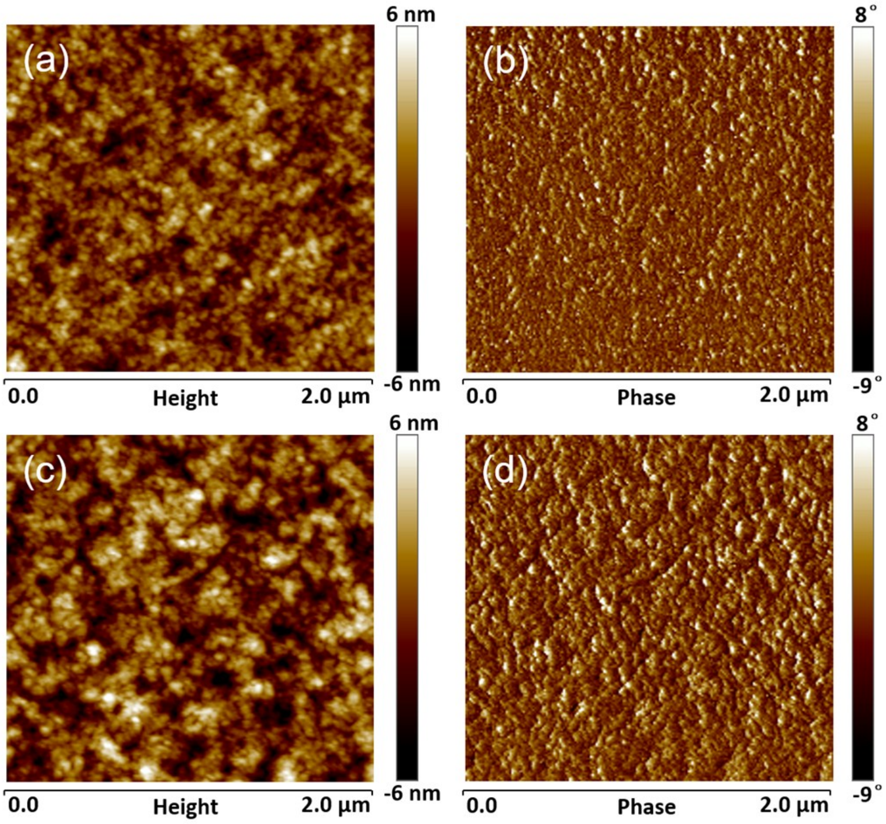

Fig. S20 AFM height (left) and phase (right) images for the blend films. (a) and (b), P1:Y6 film (R_{rms} = 1.49 nm); (c) and (d), P2:Y6 film (R_{rms} = 1.95 nm). R_{rms}: root-mean-square roughness.

Reference

[1] C. Duan, W. Cai, B. Hsu, C. Zhong, K. Zhang, C. Liu, Z. Hu, F. Huang, G. C. Bazan, A. J. Heeger and Y. Cao, *Energy Environ. Sci.*, 2013, **6**, 3022.